



Synthesis of dendritic silver nanostructures and their application in hydrogen peroxide electroreduction

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ABSTRACT

Well-defined silver (Ag) dendritic nanostructures were successfully synthesized by electrodeposition without the use of any template or surfactant. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to investigate the as-prepared Ag nanomaterials. These dendrites are aggregates of Ag nanoparticles, which are highly crystalline in nature. The concentration of AgNO₃ affects the shape of the nanoparticles. In addition, the electrochemical properties of the Ag dendrite-modified glassy carbon electrode (Ag/GC) were characterized by cyclic voltammetry and chronoamperometry. Results indicated that the as-obtained Ag dendrites exhibited favorable electroreduction activity towards oxygen (O₂) and hydrogen peroxide (H₂O₂). When used as a sensor, the Ag/GC electrode exhibited a wide linear range of 0.005–12 mM H₂O₂, with a remarkable sensitivity of 7.39 μA/mM, a detection limit of 0.5 μM, estimated at a signal-to-noise ratio of 3, and a rapid response time (within 5 s). Moreover, the electrode showed good reproducibility, anti-interferent ability and long-term stability.

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1. Introduction

Determining hydrogen peroxide (H₂O₂) has become extremely important in recent years because of its wide and varied applications in many research fields, such as in the food industry, biotechnology, the clinical practice, the pharmaceutical industry and environmental protection [1–3]. Many analytical methods have been employed for the determination of H₂O₂, including titrimetry [4], spectrophotometry [5] and chemiluminescence [6]. An alternative to these methods is to employ an electrochemical sensor, which has become a subject of considerable interest because of its low detection limit and high selectivity and sensitivity. For H₂O₂, however, the use of such an electrode is made difficult by the slow electrode kinetics on many electrode materials [7]. As a result, high overpotentials are required, placing the voltammetric wave in the same potential region as common interferences, such as ascorbic acid (AA), uric acid (UA) and acetaminophen (AP). Thus, considerable work has been devoted to the reduction of H₂O₂ at a relative low applied potential.

Noble metals, such as platinum [8–10], gold [11,12], and palladium [13], are commonly used as nanoparticles (NPs) to prepare

H₂O₂ sensors due to their large specific surface area and excellent conductivity and electrocatalytic activities. As a typical nanomaterial, silver (Ag) has recently been shown to have good catalytic activity for H₂O₂ and has attracted scientific interest [7,14–16]. Welch et al. proved that the electro-reduction of H₂O₂ occurred directly on the Ag NPs [7]. Guascito et al. reported that Ag NPs dispersed in a polyvinyl alcohol (PVA) film could facilitate H₂O₂ reduction, showing excellent catalytic activity [17]. In our previous work, Ag NPs reduced onto the surface of multi-wall carbon nanotubes were also demonstrated to have good reduction catalysis towards H₂O₂. However, to the best of our knowledge, except for the above-mentioned spherical nanoparticles, there are few reports about the catalytic ability of other Ag nanostructures for H₂O₂ reduction. It is well-known that the catalytic reactivity of metal nanomaterials depends on their morphologies [18]; therefore, it is highly desirable to try other Ag nanostructures for H₂O₂ sensor fabrication.

Because of their fascinating hierarchical structures and potential applications in the catalysis and technological fields, dendritic materials have attracted considerable attention [19–22]. As electrode modification materials, the open porous structure of the nanodendrites is critical for mass transfer, and the high surface area of the dendrite assembly is in favor of heterogeneous catalysis, both of which are important in the electrochemical reaction [20,22].

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The current methods by which Ag dendritic nanostructures can be obtained are founded mainly on electrochemical, chemical and physical means. Irradiations, chemical reagents and templates are usually used in their synthesis. For instance, Yang et al. obtained dendritic Ag nanocrystallites via γ -irradiation in an isopropyl alcohol solution [23]. Chen and co-workers produced Ag dendrites in the presence of poly(vinyl alcohol) (PVA) by a photoreduction technique [19]. Xie and co-workers synthesized Ag dendritic nanostructures using Raney nickel as both a template and a reducing agent [24]. Wen and co-workers synthesized Ag nanodendrites by suspending zinc microparticles as a heterogeneous reducing agent [25]. More recently, Han et al. [26] successfully prepared Ag dendrites via an acetone-based solvent route, and Rezaei and Damiri [27] obtained dendritic silver nanostructures with the assistance of polyethylene glycol 400 (PEG-400) as a soft template. However, most of the methods reported are complex, requiring different kinds of chemicals or templates. Furthermore, the potential of those Ag dendritic nanostructures in electrocatalytic applications has not been sufficiently studied.

Here, we report on a successful synthesis of well-defined Ag dendritic nanostructures by electrodeposition, without the addition of any template or surfactant, and the achievement of a super electrocatalyst with good electroanalysis properties. The dendritic structure was electrodeposited directly on the surface of the GC electrode. In our study, no further chemical treatment or special technique is needed to affix the catalyst onto the electrode surface. Electrodeposition is a versatile way to create new materials with high efficiency and a broad surface area, and the nanoparticle shapes and sizes can be readily controlled by adjusting the preparation conditions [28]. Therefore, firstly, Ag nanoparticles were prepared on a GC electrode under controlled conditions, and their morphology, structure, and formation mechanisms were discussed. Then, the electrocatalytic activity of the novel dendritic structures towards O_2 and H_2O_2 was evaluated with electrochemical methods, and the use of the Ag/GC electrode as the H_2O_2 sensor was studied.

2. Experimental methods

2.1. Reagents and materials

Hydrogen peroxide (30%, v/v aqueous solution) was obtained from Tianjin Eastern Chemical Reagent Company. Uric acid, ascorbic acid and acetaminophen were obtained from Tianjin Damao Chemical Reagent Co. Silver nitrate ($AgNO_3$) was purchased from Tianjin Yingda Rare Chemical Reagent Company. Aluminum oxide nanopowder was obtained from Sigma Aldrich. All other reagents were of analytical grade and used without further purification. Freshly prepared 0.1 M phosphate buffer solution (PBS, pH 7.6), consisting of Na_2HPO_4 and KH_2PO_4 , was used as the supporting electrolyte. All aqueous solutions were prepared with doubly distilled water. All experiments were performed at room temperature, approximately 25 °C.

2.2. Instrumentation

The electrochemical measurements were performed at room temperature in a conventional one-compartment cell using a 283 Potentiostat–Galvanostat electrochemical workstation (EG&G PARC with M270 software), linked to a personal computer for data acquisition and potential control. A conventional three-electrode system, comprising the Ag dendrite-modified GC electrode (3 mm diameter) as a working electrode, a Pt wire (1 mm diameter) as an auxiliary electrode and an Ag/AgCl (saturated with KCl) as a reference electrode, was employed for all electrochemical experiments.

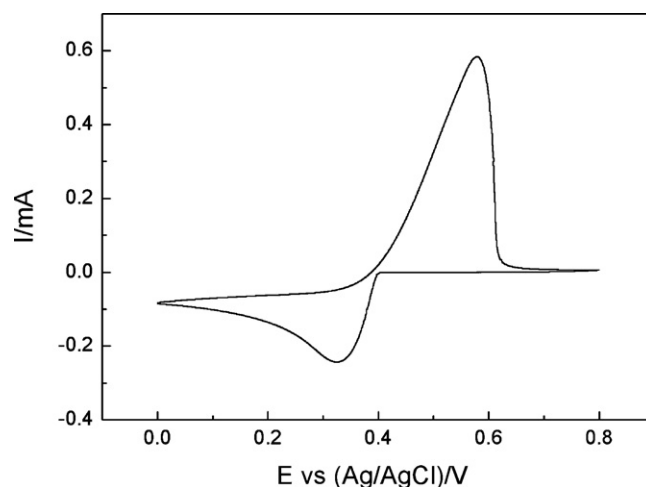


Fig. 1. Cyclic voltammograms of the GC electrode in a solution containing 10 mM $AgNO_3$ + 0.1 M KNO_3 , scan rate: 50 mV/s.

In the steady-state amperometric experiment, a magnetic stirrer provided the convective transport.

The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-rA with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) on a diffractometer (Rigaku, Japan). Scanning electron microscopy (SEM) was operated using a field emission microscope (QUANTA 200, FEI Co.). Transmission electron microscopy (TEM) images were obtained by using a Tecnai G2 F20 instrument (Philips Holland).

3. Results and discussion

3.1. Electrodeposition of Ag on a GC electrode

Cyclic voltammetry was utilized to monitor the redox behavior of Ag^+ at a GC electrode. As shown in Fig. 1, in the solution of 10 mM $AgNO_3$ and 0.1 M KNO_3 , the GC electrode showed a cathodic peak at +0.32 V and a sharp anodic peak at 0.55 V. The cathodic peak was ascribed to a reduction of Ag^+ to form atomic Ag, and the anodic peak was attributed to the stripping of the electrodeposited Ag atoms. According to the above redox behaviors, the GC electrode was electrodeposited in this solution for 60 s at -0.3 V to obtain the Ag modified electrode (Ag/GC).

3.2. Characterization of the Ag nanostructures

Cyclic voltammetry was firstly employed to characterize the nanomaterials deposited on the GC electrode. As shown in Fig. 2A, cyclic voltammograms were obtained with the modified GC electrode in 0.1 M PBS (pH 7.6). A pair of well-defined redox peaks were observed at +0.1 V and +0.4 V, respectively, which could be attributed to the Ag_2O/Ag redox couple, demonstrating the existence of Ag [29,30]. Fig. 2B shows the XRD patterns of the as-prepared samples. In the XRD spectra, the four diffraction peaks observed ($2\theta = 38.0^\circ$, 44.2° , 64.3° and 77.2°) could be indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks of the cubic structure of metallic Ag, indicating that the dendrite is crystalline Ag [31]. The presence of Pt peaks could be attributed to the slice of platinum substrate used.

Fig. 3 displays the corresponding SEM (A) and TEM (B) images of the samples, exhibiting typical and beautiful dendrites. Further observation shows that each dendrite consists of a long central backbone and sharp side branches, which preferentially grow along two definite directions rather than randomly ramified growth. Surprisingly and interestingly, the side branches, which emerged at about 60° angles with respect to the central backbone, are nearly

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